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(54) Reversible heat-sensitive recording materials

(57) A reversible heat-sensitive recording material comprises a sheet substrate having coated on the surface thereof a coating composition containing, as a chromogenic component, a heat-discoloring material comprising a homogeneous fused mixture of (A) an electron-donating chromatic organic compound; (B) a phenolic carboxylic acid or similar compound reactive with (A) to cause reversible coloring; and (C) a component for controlling the temperature and heat-sensitivity of the reaction between components (A) and (B). (A), (B) and (C) are present in a ratio of 1:0.1 to 50:1 to 800 by weight. The heat-discoloring material exhibits a coloring-color eliminating hysteresis character with a temperature width broader than 3°C and can form a positive or negative image by the application of local cooling or heating. The image formed can be stably maintained within a specific temperature range and easily erased, so that the material can be repeatedly re-used to form additional images.

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## SPECIFICATION

## Reversible heat-sensitive recording materials

This invention relates to a reversible heat-sensitive recording material. More particularly, the invention relates to a heat-sensitive recording material which can be repeatedly used by utilizing the hysteresis character of a chromogenic component, that is, which can record a positive image or a negative image by the application of local cooling or heating, stably maintain the record by keeping the recording material in a definite temperature range, and can easily erase the record, if desired, by exposing the record or the recording material to a high or low temperature, respectively.

Conventional reversible heat-sensitive recording materials which can be repeatedly used in the manner as described above include a reversible heat-sensitive recording material utilizing the heat-discoloring property of a metal complex salt such as  $\text{Ag}_2\text{Hgl}_4$  or  $\text{Cu}_2\text{Hgl}_4$  and a heat-sensitive image-indicating material (which can reversibly repeat its transparent state and white turbid state by the application of heat) comprising a matrix material composed of a thermoplastic resin, and an organic low molecular weight material dispersed in said matrix material as recently proposed by Japanese Patent Publication (unexamined) No. 89992/82. However, these materials have disadvantages such as: (1) the contrast between a recorded portion and a background portion is low, (2) optional selection of the record keeping temperature is impossible, and (3) free selection of color is impossible.

A primary object of this invention is to provide a reversible heat-sensitive recording material without the foregoing disadvantages.

According to this invention, there is provided a reversible heat-sensitive recording material using, as chromogenic components, a heat-discoloring material comprising a homogeneous fused mixture of

(A) at least one electron-donating chromatic organic compound selected from diaryl phthalides, indolyl phthalides, polyaryl carbinols, leuco auramines, acyl auramines, aryl auramines, Rhodamine B lactams, indolines, spiropyrans, and fluorans;

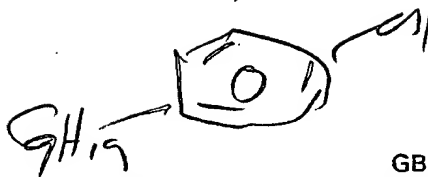
(B) at least one compound selected from phenolic compounds having 6 to 49 carbon atoms, metal salts of the phenolic compounds, aromatic carboxylic acids having 7 to 12 carbon atoms, aliphatic carboxylic acids having 2 to 5 carbon atoms, metal salts of carboxylic acids having 2 to 22 carbon atoms, acidic phosphoric esters having 1 to 44 carbon atoms, metal salts of the acidic phosphoric esters, and triazole compounds having 2 to 24 carbon atoms; and

(C) at least one compound selected from aliphatic monohydric alcohols having 4 to 31 carbon atoms, alicyclic monohydric alcohols having 5 to 10 carbon atoms, aromatic monohydric alcohols having 7 to 9 carbon atoms, polyhydric alcohols having 2 to 6 carbon atoms, ester compounds of monocarboxylic acids having 2 to 22 carbon atoms and aliphatic monohydric alcohols having 1 to 22 carbon atoms, ester compounds of monocarboxylic acids having 2 to 22 carbon atoms and phenols having 6 to 18 carbon atoms, ester compounds of monocarboxylic acids having 2 to 22 carbon atoms and polyhydric alcohols having 2 to 6 carbon atoms, ester compounds of polycarboxylic acids having 2 to 12 carbon atoms and aliphatic monohydric alcohols having 1 to 22 carbon atoms, aliphatic ketones having 5 to 35 carbon atoms, aromatic ketones having 8 to 13 carbon atoms, fatty acid amides having 2 to 22 carbon atoms, the N-alkyl-substituted compounds of the fatty acid amides, aliphatic ethers having 8 to 36 carbon atoms, aromatic ethers having 12 to 20 carbon atoms, aliphatic monocarboxylic acids having 6 to 22 carbon atoms, thiols having 10 to 18 carbon atoms, sulfides having 16 to 89 carbon atoms, disulfides having 16 to 36 carbon atoms, sulfoxides having 2 to 14 carbon atoms, and sulfones having 4 to 14 carbon atoms, as the necessary components.

Figure 1 is a graph showing the hysteresis character of the color density change caused by the temperature change of a heat-discoloring material used for the reversible heat-sensitive recording material of this invention, wherein the axis of the abscissa stands for temperature and the axis of the ordinate for color density.

As is shown in Figure 1, the heat-discoloring material used in this invention exhibits a hysteresis phenomenon which is caused by change of temperature (shown by the axis of the abscissa thereof), to repeat coloring and achromatization. In the graph of Figure 1, A is a point showing the density at the minimum temperature  $T_3$  at which the heat-discoloring material reaches a completely achromatized state, B is a point showing the density at the maximum temperature  $T_1$  at which the heat-discoloring material reaches the completely colored state, and at a temperature  $T_2$  of the heat-discoloring material, two phases of a coloring state, point C and an achromatizing state, point D coexist. The temperature region near  $T_2$ , that is, the temperature region at which the coloring state and the achromatizing state can coexist is a temperature region capable of keeping records formed on the heat-sensitive recording material of this invention. The length of the line CD is a measure showing the contrast between a record and a background and the length of line EF passing the middle point of line CD is a temperature width or range indicating the extent of the hysteresis. The broader the width, the more easily the record is maintained. According to the inventors' experiments, it has been found that the foregoing temperature width must be broader than  $3^\circ\text{C}$ , preferably broader than  $8^\circ\text{C}$  from a practical recording keeping aspect. The preferred range for the temperature width is  $2$  to  $150^\circ\text{C}$ , more preferably  $8$  to  $100^\circ\text{C}$ .

The components constituting the heat-discoloring material used in this invention are now described in detail.

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The electron-donating chromatic organic compounds used as component (A) are, as described above, diaryl phthalides, indolyl phthalides, polyaryl carbinols, leuco auramines, acyl auramines, aryl auramines, Rhodamine B lactams, indolines, spiropyran, and fluorans.

Practical examples of these compounds are Crystal Violet lactone, Malachite Green lactone,

- 5 Michler's hydrol, Crystal Violet carbinol, Malachite Green carbinol, N-(2,3-dichlorophenyl)leuco auramine, N-benzoyl auramine, Rhodamine B lactam, N-acetyl auramine, N-phenyl auramine, 2-(phenyliminoethylidene)-3,3-dimethylindoline, N-3,3-trimethylindolinobenzspiropyran, 8-methoxy-N-3,3-trimethylindolinobenzspiropyran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-7-methoxyfluoran, 3-diethylamino-6-benzyloxyfluoran, 1,2-benz-6-diethylaminofluoran, 3,6-di-p-toluidino-4,5-dimethylfluoran-phenylhydrazido-p-lactam, 3-amino-5-methylfluoran, 2-methyl-3-amino-6-methyl-7-methylfluoran, 2,3-butylene-6-di-n-butylaminofluoran, 3-diethylamino-7-anilino-10 fluoran, 3-diethylamino-7-(p-toluidino)fluoran, 7-acetamino-3-diethylaminofluoran, 2-bromo-6-cyclohexylaminofluoran and 2,7-dichloro-3-methyl-6-n-butylaminofluoran; preferably Crystal Violet lactone, Malachite Green lactone, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-7-methoxyfluoran, 3-diethylamino-6-benzyloxyfluoran, 1,2-benz-6-diethylaminofluoran, 3,6-di-p-toluidino-4,5-dimethylfluoran-phenylhydrazido-p-lactam, 3-amino-5-methylfluoran, 2-methyl-3-amino-6-methyl-7-methylfluoran, 2,3-butylene-6-di-n-butylaminofluoran, 3-diethylamino-7-anilino-15 fluoran, 3-diethylamino-7-(p-toluidino)fluoran, 7-acetamino-3-diethylaminofluoran, 2-bromo-6-cyclohexylaminofluoran and 2,7-dichloro-3-methyl-6-n-butylaminofluoran.
- 20 The compounds used as component (B) in this invention are, as described above, phenolic compounds having 6 to 49 carbon atoms, metal salts of the phenolic compounds, aromatic carboxylic acids having 7 to 12 carbon atoms, aliphatic carboxylic acids having 2 to 5 carbon atoms, metal salts of carboxylic acids having 2 to 22 carbon atoms, acidic phosphoric esters having 1 to 44 carbon atoms, metal salts of the acidic phosphoric esters, and triazole compounds having 2 to 24 carbon atoms.
- 25 Useful phenolic compounds in the compounds of component (B) include monophenols and polyphenols, which may have a substituent such as an alkyl group, an aryl group, an acyl group, an alkoxy, carbonyl group or a halogen atom. Practical examples of these phenolic compounds are tert-butylphenol, nonylphenol, dodecylphenol, styrenated phenol, 2,2-methylenebis(4-methyl-6-tert-butylphenol),  $\alpha$ -naphthol,  $\beta$ -naphthol, hydroquinone monomethyl ether, guaiacol, eugenol, p-chlorophenol, p-bromophenol, o-chlorophenol, o-bromophenol, o-phenylphenol, p-phenylphenol, p-(p-chlorophenyl)phenol, o-(o-chlorophenyl)phenol, methyl p-oxybenzoate, ethyl p-oxybenzoate, propyl p-oxybenzoate, butyl p-oxybenzoate, octyl p-oxybenzoate, dodecyl p-oxybenzoate, 3-isopropyl catechol, p-tert-butyl catechol, 4,4-methyldiphenol, 4,4-thiobis(6-tert-butyl-3-methylphenol), 1,1-bis(4-hydroxyphenyl)cyclohexane, 4,4-butylidenebis(6-tert-butyl-3-methylphenol), bisphenol A, bisphenol S, 35 1,2-dioxynaphthalene, chlorocatechol, bromocatechol, 2,4-dihydroxybenzophenone, phenolphthalein, o-cresolphthalein, methyl protococatechuate, ethyl protococatechuate, propyl protococatechuate, octyl protococatechuate, dodecyl protococatechuate, 2,4,6-trioxymethylbenzene, 2,3,4-trioxyethylbenzene, methyl gallate, ethyl gallate, propyl gallate, butyl gallate, hexyl gallate, octyl gallate, dodecyl gallate, cetyl gallate, stearyl gallate, 2,3,5-trioxynaphthalene, tannic acid and phenol-formaldehyde prepolymer; preferably tert-butylphenol, nonylphenol, dodecylphenol, p-phenylphenol, p-(p-chlorophenyl)phenol, methyl p-oxybenzoate, ethyl p-oxybenzoate, propyl p-oxybenzoate, butyl p-oxybenzoate, octyl p-oxybenzoate, dodecyl p-oxybenzoate, 4,4-methyldiphenol, 4,4-thiobis(6-tert-butyl-3-methylphenol), 1,1-bis(4-hydroxyphenyl)cyclohexane, 4,4-butylidenebis(6-tert-butyl-3-methylphenol), bisphenol A and bisphenol S.
- 40 Metal salts of the foregoing phenolic compounds include salts of the phenolic compounds with metals such as sodium, potassium, lithium, calcium, zinc, zirconium, aluminum, magnesium, nickel, cobalt, tin, copper, iron, vanadium, titanium, lead and molybdenum.
- 45 Examples of aromatic carboxylic acids having 7 to 12 carbon atoms and the aliphatic carboxylic acids having 2 to 5 carbon atoms in the compounds of component (B) include maleic acid, fumaric acid, benzoic acid, toluic acid, p-tert-butylbenzoic acid, chlorobenzoic acid, bromobenzoic acid, ethoxybenzoic acid, gallic acid, naphthoic acid, phthalic acid, naphthalenedicarboxylic acid, acetic acid, propionic acid, butyric acid and valeric acid; preferably benzoic acid, toluic acid, p-tert-butylbenzoic acid, chlorobenzoic acid, bromobenzoic acid, ethoxybenzoic acid, butyric acid and valeric acid.
- 50 Examples of metal salts of carboxylic acids having 2 to 22 carbon atoms in the compounds of component (B) include metal salts of monocarboxylic acids and polycarboxylic acids. Practical examples of these salts are the metal (such as sodium, potassium, lithium, calcium, zinc, zirconium, aluminum, magnesium, nickel, cobalt, tin, copper, iron, vanadium, titanium, lead and molybdenum acid; salts of acetic acid, propionic acid, butyric acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, behenic acid, crotonic acid, oleic acid, elaidic acid, linolic acid, linolenic acid, monochloroacetic acid, monobromoacetic acid, monofluoroacetic acid, glycolic acid, hydroxypropionic acid, hydroxybutyric acid, ricinolic acid, 1,2-hydroxystearic acid, lactic acid, pyruvic acid, oxalic acid, malonic acid, succinic acid, adipic acid, sebacic acid, malic acid, tartaric acid, valeric acid, maleic acid, fumaric acid, naphthenic acid, benzoic acid, toluic acid, phenylacetic acid, p-tert-butylbenzoic acid, cinnamic acid, chlorobenzoic acid, bromobenzoic acid, ethoxybenzoic acid, mandelic acid, protocatechuric acid, vanillic acid, resorcinic acid, dioxybenzoic acid, dioxychlorobenzoic acid, 65

gallic acid, naphthoic acid, hydroxynaphthoic acid, phthalic acid, phthalic monoethyl ester, naphthalenedicarboxylic acid, naphthalenedicarboxylic acid monomethyl ester, trimellitic acid and pyromellitic acid; preferably metal (such as sodium, potassium, lithium, calcium, zinc, and nickel) salts of butyric acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, linolic acid, succinic acid, adipic acid, sebacic acid, malic acid, benzoic acid, toluic acid, p-tert-butylbenzoic acid, chlorobenzoic acid, bromobenzoic acid and ethoxybenzoic acid.

Examples of acidic phosphoric esters having 1 to 44 carbon atoms in the compounds of component (B) include acidic phosphoric ester compounds having an ester group such as an alkyl group, a branched alkyl group, an alkenyl group, an alkynyl group, a cycloalkyl group or an aryl group, and the derivatives of these groups. The preferred ester groups are an alkyl group, a branched alkyl group, a cycloalkyl group and an aryl group. Examples of acidic phosphoric ester compounds include monoesters and diesters, or the mixtures of these esters. In the following practical examples, a mixture of the monomer and the diester is referred to as an acid phosphate.

Practical examples of the acidic phosphoric ester compounds are methyl acid phosphate, ethyl acid phosphate, n-propyl acid phosphate, n-butyl acid phosphate, 2-ethylhexyl acid phosphate, n-octyl acid phosphate, isodecyl acid phosphate, n-decyl acid phosphate, lauryl acid phosphate, myristyl acid phosphate, cetyl acid phosphate, stearyl acid phosphate, docosyl acid phosphate, oleyl acid phosphate, 2-chloroethyl acid phosphate, 2,3-dibromo-2,3-dichloropropyl acid phosphate, dichloropropyl acid phosphate, cyclohexyl acid phosphate, phenyl acid phosphate, o-tolyl acid phosphate, 2,3-xylyl acid phosphate, p-cumenyl acid phosphate, mesityl acid phosphate, 1-naphthyl acid phosphate, 2-naphthyl acid phosphate, 1-anthryl acid phosphate, benzyl acid phosphate, phenethyl acid phosphate, styryl acid phosphate, cinnamyl acid phosphate, triethyl acid phosphate, phenyl methyl phosphate, phenyl ethyl phosphate, phenyl n-propyl phosphate, phenyl n-butyl phosphate, phenyl n-octyl phosphate, phenyl lauryl phosphate, phenyl cyclohexyl phosphate, phenyl 2,3-xylyl phosphate, cyclohexyl stearyl phosphate, cyclohexyl cetyl phosphate, dimethyl phosphate, diethyl phosphate, di-n-propyl phosphate, di-n-butyl phosphate, di-n-hexyl phosphate, di(2-ethylhexyl) phosphate, di-n-decyl phosphate, dilauryl phosphate, dimyristyl phosphate, dicetyl phosphate, distearyl phosphate, dibehenyl phosphate, diphenyl phosphate, dicyclohexyl phosphate, di-o-tolyl phosphate, bis(diphenylmethyl) phosphate, bis(triphenylmethyl) phosphate, di(2,3-xylyl) phosphate, dibenzyl phosphate, and di(1-naphthyl) phosphate; preferably 2-ethylhexyl acid phosphate, n-octyl acid phosphate, isodecyl acid phosphate, n-decyl acid phosphate, lauryl acid phosphate, myristyl acid phosphate, cetyl acid phosphate, stearyl acid phosphate, docosyl acid phosphate, cyclohexyl acid phosphate, phenyl acid phosphate, o-tolyl acid phosphate, phenyl n-butyl phosphate, phenyl n-octyl phosphate, phenyl lauryl phosphate, phenyl 2,3-xylyl phosphate, cyclohexyl stearyl phosphate, cyclohexyl cetyl phosphate, di-n-butyl phosphate, di-n-hexyl phosphate, di(2-ethylhexyl) phosphate, di-n-decyl phosphate, dilauryl phosphate, dimyristyl phosphate, dicetyl phosphate, distearyl phosphate, dibehenyl phosphate, diphenyl phosphate, dicyclohexyl phosphate and di-o-tolyl phosphate.

Examples of metal salts of the acidic phosphoric esters include metal (such as sodium, potassium, lithium, calcium, zinc, zirconium, aluminum, magnesium, nickel, cobalt, tin, copper, iron, vanadium, titanium, lead and molybdenum salts of the foregoing acidic phosphoric ester compounds.

Practical examples of the triazole compounds having 2 to 24 carbon atoms in the compounds of component (B) are 1,2,3-triazole, 4(5)-hydroxy-1,2,3-triazole, 5(6)-methyl-1,2,3-benzotriazole, 5-chloro-1,2,3-benzotriazole, 7-nitro-1,2,3-benzotriazole, 4-benzoylamino-1,2,3-benzotriazole, 4-hydroxy-1,2,3-benzotriazole, naphtho-1,2,3-triazole, 5,5'-bis(1,2,3-benzotriazole) and 1,2,3-benzotriazole-4-sulfooctylamide.

Also, the compounds used as component (C) in this invention are, as described above, aliphatic monohydric alcohols having 4 to 31 carbon atoms, alicyclic monohydric alcohols having 5 to 10 carbon atoms, aromatic monohydric alcohols having 7 to 9 carbon atoms, polyhydric alcohols having 2 to 6 carbon atoms, ester compounds of monocarboxylic acids having 2 to 22 carbon atoms and aliphatic monohydric alcohols having 1 to 22 carbon atoms, ester compounds of said monocarboxylic acids and phenols having 6 to 18 carbon atoms, ester compounds of said monocarboxylic acids and polyhydric alcohols having 2 to 6 carbon atoms, ester compounds of polycarboxylic acids having 2 to 12 carbon atoms and aliphatic monohydric alcohols having 1 to 22 carbon atoms, aliphatic ketones having 5 to 35 carbon atoms, aromatic ketones having 8 to 13 carbon atoms, fatty acid amides having 2 to 22 carbon atoms, the N-alkyl-substituted compounds of the fatty acid amides, aliphatic ethers having 8 to 36 carbon atoms, aromatic ethers having 12 to 20 carbon atoms, aliphatic monocarboxylic acids having 6 to 22 carbon atoms, thiols having 10 to 18 carbon atoms, sulfides having 16 to 89 carbon atoms, disulfides having 16 to 36 carbon atoms, sulfoxides having 2 to 14 carbon atoms, and sulfones having 4 to 14 carbon atoms.

Examples of alcohols in the compounds of component (C) include monohydric alcohols, polyhydric alcohols, and the derivatives thereof. Practical examples of these alcohols are n-octyl alcohol, n-nonyl alcohol, n-decyl alcohol, n-lauryl alcohol, n-myristyl alcohol, n-cetyl alcohol, n-stearyl alcohol, n-eicosyl alcohol, n-docosyl alcohol, n-melissyl alcohol, isocetyl alcohol, isostearyl alcohol, isodocosyl alcohol, oleyl alcohol, cyclohexanol, cyclopentanol, benzyl alcohol, cinnamyl alcohol, ethylene glycol, diethylene

5 benzyl alcohol.	5
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10 methyl myristate, ethyl myristate, butyl myristate, hexyl myristate, octyl myristate, lauryl myristate,	10
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20 preferably amyl acetate, octyl acetate, butyl propionate, octyl propionate, phenyl propionate, ethyl 20

30 butyl ketone, methyl hexyl ketone, mesityl oxide, cyclohexanone, methyl cyclohexanone, acetophenone, 30

35 ether, ethylene glycol diethyl ether, diethylene glycol diethyl ether, ethylene glycol diphenyl ether and 35

40 amide, lauric acid amide, myristic acid amide, palmitic acid amide, stearic acid amide, behenic acid 40

65 Practical examples of the aliphatic carboxylic acids having 6 to 22 carbon atoms in the 65

compounds of component (C) are caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid, isomyristic acid, isopalmitic acid, isostearic acid, oleic acid, elaidic acid, linolic acid, linolenic acid, eleostearic acid, arachidonic acid, 2-oxylauric acid, 2-oxymyristic acid, 2-oxypalmitic acid, 2-oxystearic acid, 3-oxystearic acid, 12-hydroxystearic acid, ricinoleic acid, 2-bromolauric acid, 2-bromomyristic acid, 2-bromopalmitic acid, 2-bromostearic acid, 18-bromostearic acid, 2-chlorostearic acid, 18-chlorostearic acid, dioxypalmitic acid, dioxystearic acid, 3-ethyl-3-lauryl-3-oxypropionic acid, 2-methyl-3-oxystearic acid, 2-ketostearic acid, 2-ketopalmitic acid, azelaic acid monoethyl ester, azelaic acid monobutyl ester, azelaic acid monoethyl ester, sebacic acid monoethyl ester, sebacic acid monobutyl ester, sebacic acid monoethyl ester, sebacic acid monolauryl ester, 1,12-dodecamethylenedicarboxylic acid, 1,14-tetradecamethylenedicarboxylic acid, 1,16-hexadecamethylenedicarboxylic acid and dimer acid; preferably caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, 12-hydroxystearic acid, 2-bromolauric acid, 2-bromomyristic acid, 2-bromopalmitic acid, 2-bromostearic acid, 18-bromostearic acid, 2-chlorostearic acid and 18-chlorostearic acid.

Practical examples of the thiols in the compounds of component (C) are n-decyl mercaptan, n-dodecyl mercaptan, m-myristyl mercaptan, n-cetyl mercaptan, n-stearyl mercaptan, isododecyl mercaptan, isomyristyl mercaptan, isocetyl mercaptan and dodecyl benzyl mercaptan.

Practical examples of the sulfides in the compounds of component (C) are di-n-octyl sulfide, di-n-nonyl sulfide, di-n-decyl sulfide, di-n-dodecyl sulfide, di-n-myristyl sulfide, di-n-cetyl sulfide, di-n-stearyl sulfide, di-tert-dodecyl sulfide, octyldodecyl sulfide, diphenyl sulfide, dibenzyl sulfide, ditolyl sulfide, diethylphenyl sulfide, 4,4-dichlorodiphenyl sulfide, dialauryl thiopropionate, distearyl thiodipropionate, tetra(laurylthiopropionic acid) pentaerythritol ester, and tetra(stearylthiopropionic acid) pentaerythritol; preferably di-n-octyl sulfide, di-n-nonyl sulfide, di-n-decyl sulfide, di-n-dodecyl sulfide, di-n-myristyl sulfide, di-n-cetyl sulfide, di-n-stearyl sulfide, di-tert-dodecyl sulfide, octyldodecyl sulfide, diphenyl sulfide and dibenzyl sulfide.

Practical examples of the disulfides in the compounds of component (C) are di-n-decyl disulfide, di-n-dodecyl disulfide, di-n-myristyl disulfide, di-n-cetyl disulfide, di-n-stearyl disulfide, diphenyl disulfide, dibenzyl disulfide, ditolyl disulfide, dinaphthyl disulfide and 4,4-dichlorodiphenyl disulfide; preferably di-n-decyl disulfide, di-n-dodecyl disulfide, di-n-myristyl disulfide, di-n-cetyl disulfide, di-n-stearyl disulfide and diphenyl disulfide.

Practical examples of the sulfoxides in the compounds of component (C) are dimethyl sulfoxide, diethyl sulfoxide, tetramethylene sulfoxide, diphenyl sulfoxide and dibenzyl sulfoxide; preferably diphenyl sulfoxide and dibenzyl sulfoxide.

Also, practical examples of the sulfones in the compounds of component (C) are diethylsulfone, dibutylsulfone, methylphenylsulfone, diphenylsulfone, ditolylsulfone, dibutylphenylsulfone, dibenzylsulfone and dichlorodiphenylsulfone; preferably diphenylsulfone, ditolylsulfone, dibutylphenylsulfone and dibenzylsulfone.

The heat-discoloring material used in this invention is obtained by mixing foregoing three components (A), (B) and (C) in a mixing ratio of 1:0.1 to 50:1 to 800 by weight ratio, preferably 1:1 to 20:10 to 400, more preferably 1:2 to 15:20 to 200, and fusing the mixture by heating at a temperature of 50 to 150°C, preferably 80 to 120°C, to form a homogeneous fused mixture.

Component (A) used in this invention is for determining the coloring color of the heat-discoloring material, component (B) is for reversibly causing coloring by causing a reaction with component (A), and component (C) is for controlling the temperature and heat-sensitivity for the foregoing reaction. The extent of the hysteresis character of the heat-discoloring material of this invention for coloring and achromatization depends upon the kind of each of the components described above but said mixing ratio of these components is the dominant factor for said extent. In general, the foregoing discoloring temperature range is near the melting point of component (C) and hence a heat-discoloring material showing a desired discoloring temperature range and color-keeping temperature range is obtained by using a suitable combination of compounds having different respective melting points.

As described above, the heat-discoloring material of this invention exhibits the hysteresis phenomenon in proportion to the temperature change as shown in the graph of Figure 1 to repeat coloring and achromatization but when the acidic phosphoric ester or the metal salt thereof is used as component (B), the graph takes a form whereby it is rotated 180° with respect to the CD line as the axis. In other words, the heat-discoloring material is in a colored state on the high temperature side and in an achromatized state on the low temperature side.

The reversible heat-sensitive recording material is prepared by fusing the foregoing heat-discoloring material by heating, and coating the fused composition in an amount of about 1 to 50 g/m<sup>2</sup> on the surface of a sheet base such as a paper, a plastic film, a cloth, and a metal foil, preferably a paper or a plastic film, or by encapsulating the heat-discoloring material in microcapsules having a diameter smaller than 30 μm, preferably 1 to 10 μm, by a well-known capsulation method (such as a coacervation method as described in U.S. Patents 2,800,457 and 3,116,206, an interfacial polymerization method as described in U.S. Patents 3,429,827 and 3,167,602 or an *in situ* polymerization method as described in British Patent 989,264 dispersing the microcapsules thus

obtained into a resin solution, a resin emulsion, or a mixture thereof, and coating the coating composition thus obtained on the surface of the foregoing sheet base. Suitable methods for coating the coating composition on the surface of the sheet base include a bar coating method, a screen printing method, a gravure painting method, a flexographic printing method and an offset printing method.

5 The following Examples are intended to illustrate the present invention but not to limit it in any way. 5

#### EXAMPLE 1

After fusing 4 g of Crystal Violet lactone, 20 g of bisphenol A, and 100 g of myristyl alcohol by heating at about 100°C to form a homogeneous fused composition, the fused composition was 10 uniformly coated on a wood free paper (high-grade paper) to provide a recording sheet. The recording sheet was heated to 45°C to bring the coated layer into a white state and then the recording sheet was pressed by a rubber relief cooled to 15°C under the condition of room temperature (27°C), whereby a blue positive image was clearly exhibited. When the recording sheet was allowed to stand for 24 hours at room temperature of 25 to 30°C, the image remained stable. Then, when the recording sheet having 15 the blue image was uniformly heated to 40°C, the image was eliminated to provide a uniformly white surface. The foregoing formation and elimination steps for images could be repeatedly performed.

#### EXAMPLE 2

A mixture of 6 g of 3-diethylamino-7,8-benzofluoran (ECOC (1)), 16 g of zinc salt of bisphenol A, 20 50 g of cyclododecanol, and 50 g of cetyl alcohol was fused by heating at about 100°C to provide a homogeneous fused composition. The fused composition was uniformly coated on a coated paper, and then a polypropylene film of 20  $\mu\text{m}$  in thickness was laminated thereon to provide a recording sheet. The recording sheet thus prepared was uniformly cooled to 10°C to color the whole surface pink and then allowed to stand at 25°C. When a letter was written on the sheet by a heat pen the point of which was kept at about 50°C, a white negative image having a high contrast was formed with a pink 25 background and the image could be maintained for a desired period of time.

Then, the recording sheet was heated to 50°C to whiten the whole surface followed by allowing the sheet to cool to 25°C and when a letter was written thereon by a cold pen the point of which was kept at about 10°C, a pink positive image having a high contrast was formed with the white background. The image could be maintained for a desired period of time. As described above, the 30 formation and elimination of both the positive image and the negative image could be repeated any number of times desired.

Information relating to the recording materials of Examples 3 to 8 including the components used, the composition ratio, the recording temperature, the keeping temperature for the images, the eliminating temperature, and the colored color are shown in Table 1.

35 In these Examples, the recording materials were produced in the same manner as in Example 1 using the components shown in Table 1. 35

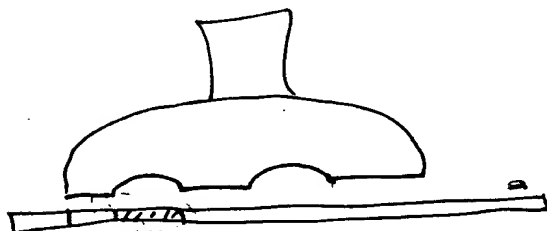




TABLE 1

Example No.	Component (A)	Heat-Discoloring Material Composition		Temperature (°C) and (color)		
		Component (B)	Component (C)	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>
3	ECOC (2) (6 g)	4,4'-Thiobis(6-t-butyl-3-methylphenol) (16 g)	Myristyl alcohol (50 g) Butanetetracarboxylic acid tetralauryl ester (50 g)	0 (black)	20	35 (white)
4	ECOC (3) (6 g)	p-Oxybenzoic acid octyl ester (16 g)	Trilaurin (100 g)	5 (pink)	25	45 (white)
5	ECOC (4) (4 g) ECOC (1) (4 g)	4,4'-Thiobis(6-t-butyl-3-methylphenol) (20g)	Myristyl alcohol (50 g) Myristyl caprate (50 g)	0 (red)	15	30 (white)
6	ECOC (5) (6 g)	5-Chloro-1,2,3-benzotriazole (16 g)	Lauron (100 g)	40 (vermillion)	58	70 (white)
7	ECOC (6) (6 g)	2,3-Xylyl acid phosphate (15 g)	Cetyl alcohol (100 g)	25 (white)	40	60 (dark red)
8	ECOC (7) (6 g)	1,1-Bis(4-hydroxyphenyl)-cyclohexane (15 g)	Diphenyl sulfide (100 g)	30 (green)	45	65 (white)

(Note): T<sub>1</sub>, T<sub>2</sub> and T<sub>3</sub> are shown in the graph of Figure 1.

ECOC: electron-donating chromatic organic compound

ECOC (1): 3-diethylamino-7,8-benzofluoran

ECOC (2): 6'-(cyclohexylmethylamino)-3'-methyl-2'-(phenylamino)-spiro[isobenzofuran-1(3H),9'-(9H)-xanthen]-3-one

ECOC (3): 3,3-bis(1-ethyl-2-methyl-1H-indol-3-yl)-1(3H)isobenzofuranone

ECOC (4): 3-chloro-6-cyclohexylaminofluoran

ECOC (5): 3-diethylamino-6-methyl-7-chlorofluoran

ECOC (6): 2'-[bis(phenylmethyl)amino]-3'-methyl-6'-(diethylamino)-spiro[isobenzofuran-1(3H),9'-(9H)-xanthen]-3-one

ECOC (7): 3-diethylamino-5-methyl-7-dibenzylaminofluoran

#### EXAMPLE 9

A mixture of 6 g of 2'-[(4-n-butylphenyl)-amino]-3'-methyl-6'-(diethylamino)-spiro[isobenzofuran-1(3H),9'-(9H)xanthen]-3-one (ECOC (8)), 15 g of bisphenol S, 60 g of stearyl alcohol, and 40 g of trimyristin was fused by heating at about 120°C to provide a homogeneous fused mixture, which was capsulated by a well-known coacervation method. Then, 80 g of the microcapsules containing the heat-discoloring material thus prepared was dispersed in a vehicle composed of 200 g of an ethylene-vinyl acetate copolymer emulsion (solid content: 50%, the lowest film-forming temperature: 0°C), 40 g of sodium alginate, and 80 g of water, the dispersion was uniformly coated on a polyester film of 25 μm in thickness and a polypropylene film of 20 μm in thickness was laminated thereon to provide a recording sheet.

When an image was recorded on the recording sheet by means of a thermal head for heat recording and immediately kept on a warm panel maintained at 40°C, a black and white negative image having high contrast was obtained and the image could be stably maintained for a desired period of time. Then, when the recording sheet was passed from the warm panel through a heating zone of 60°C and then through a cooling zone of 10°C; a reversal image was recorded thereon by means of a thermal head; and the recording sheet was kept on a warm panel, a black and white positive image having high contrast was obtained and the image could be maintained for a desired period of time. The cycle of the image formation, image keeping, and image elimination could be repeated many times.

#### 20 EXAMPLE 10

A mixture of 5 g of 6'-(diethylamino)-2'-(cyclohexyl(phenylmethyl)amino)-spiro[isobenzofuran-1(3H),9'-(9H)xanthen]-3-one (ECOC (9)), 15 g of zinc benzoate, and 100 g of di-n-hexyl ketone was fused by heating at about 100°C to provide a homogeneous fused mixture, which was capsulated by a well-known coacervation method. Then, 80 g of the microcapsules containing the heat-discoloring material thus prepared was dispersed in a vehicle composed of 200 g of a styrene-maleic acid copolymer (molecular weight: about 8,000, acid value: 170 to 185), 20 g of 28% aqueous ammonia, and 40 g of water and the dispersion was coated on a wood free paper (high-grade paper) to provide a recording sheet. The recording sheet was once heated to 30°C to whiten the whole surface and when a



letter was recorded thereon at a temperature range of 10 to 15°C, by means of a cold pen the point of which was kept at 0°C, a green positive image having high contrast was obtained with white background and the image could be maintained for a desired period of time. Then, when the recording sheet was heated again to 30°C, the whole sheet became white and the recording and eliminating steps could be repeated many times.

As described above, it will be appreciated that, according to the present invention, a recording material exhibiting a desired color and desired recording, image-keeping and image-eliminating temperatures, can be obtained by suitably selecting the composition of the heat-discoloring material used for the recording material; such a feature has never been provided by conventional recording materials of the same kind. In particular, a recording material having an image-keeping temperature within a normal temperature range has a high utility value. Also, when the contrast between a record or image and a background is expressed by the lightness difference (corresponding to the length of line CD in the graph of Figure 1), pure white being indicated by 10 and deep black by 0, the contrast of a conventional recording material (yellow-orange color change) using the metal complex salt  $\text{Ag}_2\text{Hgl}_4$  is about 1.0 to 1.1, while the contrast of the recording material of this invention is as high as 6.5 to 7.0 in black with a white background, about 5.0 in blue with a white background, and about 4.0 in red with a white background.

The reversible heat-sensitive recording material of this invention can, as a matter of course, be used as a heat-sensitive recording material having the faculty of repeating recording and elimination as well as be utilized as a heat-sensitive indicating material for thermal display.

Also, the reversible heat-sensitive recording material can be used as a writing plate using a combination of a cooling pen and a heating eraser or a combination of a heating pen and a cooling eraser. Furthermore, the recording material of this invention can be also used as a toy such as, for example, a writing plate which can be used in the bath utilizing the temperature difference between warm water and cold water. Still further, the recording material of this invention can also be incorporated in a recording device utilizing a laser light.

Moreover, since a color design can be repeatedly changed for amusement by utilizing the property of the reversible heat-sensitive recording material of this invention, the invention can be applied to the fields of personal ornaments and clothing such as neckties, T-shirts, trainers, blouses, gloves and ski-wear; and decorations such as ribbon flowers, wall tapestries and curtains.

A substantially transparent layer may be formed on the layer of coating composition.

## CLAIMS

1. A reversible heat-sensitive recording material comprising a sheet substrate having coated on the surface thereof a layer of coating composition containing, as a chromogenic component, a heat-discoloring material comprising a homogeneous fused mixture of

(A) an electron-donating chromatic organic compound selected from diaryl phthalides, indolyl phthalides, polyaryl carbinols, leuco auramines, acyl auramines, aryl auramines, Rhodamine B lactams, indolines, spiropyrans and fluorans;

(B) a compound selected from phenolic compounds having 6 to 49 carbon atoms, metal salts of such phenolic compounds, aromatic carboxylic acids having 7 to 12 carbon atoms, aliphatic carboxylic acids having 2 to 5 carbon atoms, metal salts of carboxylic acids having 2 to 22 carbon atoms, acidic phosphoric esters having 1 to 44 carbon atoms, metal salts of such acidic phosphoric esters, and triazole compounds having 2 to 24 carbon atoms; and

(C) a compound selected from aliphatic monohydric alcohols having 4 to 31 carbon atoms, alicyclic monohydric alcohols having 5 to 10 carbon atoms, aromatic monohydric alcohols having 7 to 9 carbon atoms, polyhydric alcohols having 2 to 6 carbon atoms, ester compounds of monocarboxylic acids having 2 to 22 carbon atoms and aliphatic monohydric alcohols having 1 to 22 carbon atoms, ester compounds of monocarboxylic acids having 2 to 22 carbon atoms and phenols having 6 to 18 carbon atoms, ester compounds of monocarboxylic acids having 2 to 22 carbon atoms and polyhydric alcohols having 2 to 6 carbon atoms, ester compounds of polycarboxylic acids having 2 to 12 carbon atoms and aliphatic monohydric alcohols having 1 to 22 carbon atoms, aliphatic ketones having 5 to 35 carbon atoms, aromatic ketones having 8 to 13 carbon atoms, fatty acid amides having 2 to 22 carbon atoms, the N-alkyl-substituted compounds of such fatty acid amides, aliphatic ethers having 8 to 36 carbon atoms, aromatic ethers having 12 to 20 carbon atoms, aliphatic monocarboxylic acids having 6 to 22 carbon atoms, thiols having 10 to 18 carbon atoms, sulfides having 16 to 89 carbon atoms, disulfides having 16 to 36 carbon atoms, sulfoxides having 2 to 14 carbon atoms, and sulfones having 4 to 14 carbon atoms,

the components (A), (B) and (C) being present in a weight ratio of 1:0.1 to 50:1 to 800 and the heat-discoloring material exhibiting a coloring-color eliminating hysteresis character with a temperature width broader than 3°C.

2. A material as claimed in Claim 1, in which the heat-discoloring material is contained in microcapsules having a diameter of 30  $\mu\text{m}$  or less.

3. A material as claimed in Claim 1 or 2 and additionally comprising a substantially transparent layer formed on the layer of coating composition.

4. A material as claimed in any preceding claim in which the heat-discoloring material exhibits a coloring-color eliminating hysteresis character with a temperature width broader than 8°C.

5 5. A material as claimed in any preceding claim in which said weight ratio is 1:1 to 20:10 to 400. 5

6. A material as claimed in Claim 5, in which said weight ratio is 1:2 to 15:20 to 400.

7. A material as claimed in any preceding claim, in which the components (A), (B) and (C) are selected from the compounds specifically exemplified herein.

8. A material as claimed in Claim 1 and substantially as herein described.

10 9. A reversible heat-sensitive recording material substantially as herein described with reference to any one of Examples 1 to 10. 10

10. A material as claimed in any preceding claim and bearing a positive or negative image produced by local heating or cooling.

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